An Examination of the Lighter Constituents of Air.

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(Communicated by Sir William Ramsay, F.R.S. Received November 29,—Read December 13, 1906.)

This research was undertaken with the object of ascertaining whether a large quantity of air, if systematically fractionated, would yield any constituent lighter than helium. It has been stated that "coronium" has revealed its presence in the gases emitted from the Solfatara of Pozzuoli by a line of wave-length 531·5—531·6; and that from some of the Vesuvian fumaroles gases have been obtained which give rise to new lines not coincident with any important lines in the neon or helium spectra.* Again, it has been stated by Dewar in a lecture delivered at the Royal Institution (April 11, 1902),† that in the most volatile part of the atmosphere "a vast number of rays, generally less brilliant, are distributed through the whole length of the visible spectrum. The greater part of these rays are of, as yet, unknown origin."‡

A subsidiary object of the present research was to form a new estimate of the proportion of free hydrogen in air by the method of fractionation. The most important estimations have been made by Gautier, Rayleigh, and Dewar. Gautier, using the method of passing air over red-hot copper oxide, found 19·5 volumes of free hydrogen in 100,000 volumes of air, *i.e.*, about half as much free hydrogen as carbon dioxide.§ Rayleigh‖ discussed and, in part, repeated the work of Gautier; he considered three parts per 100,000 as a maximum estimate, but regarded the question as still unsettled. Dewar, in the lecture mentioned above, stated that "air contains as a minimum not more than $\frac{1}{100000}$th of free hydrogen."

The conclusions arrived at in this paper may be briefly stated: (1) there are no unknown lines in the spectrum of the lightest portions of the air, all those observed being traceable to helium, neon, and hydrogen; (2) the amount of hydrogen separable from air is much less than the maximum assigned by the above-mentioned investigators, for it amounts to about one volume per million and a-half volumes of air.

The first stage in the fractionation was effected by means of the air-

* Nasini, Anderlini, and Salvadori, 'Accad. dei Lincei,' 1898, vol. 7, pp. 73—74.

† 'Proc. R. Inst.,' vol. 17, p. 225.

‡ See also Dewar and Liveing, 'Roy. Soc. Proc.,' vol. 67, p. 467, 1900, "Spectrum of the More Volatile Gases of the Atmosphere Condensed at the Temperature of Liquid Hydrogen. Preliminary Notice."

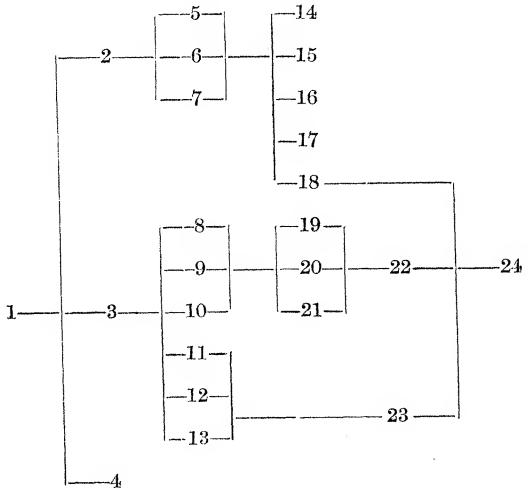
§ 'Ann. Chim. Phys.,' vol. 22, 1901.

‖ 'Phil. Mag.,' vol. 3, 1902, p. 416.

liquefying apparatus at University College, Gower Street. The air of the compressor room (situated in the basement and well ventilated) passed through the apparatus, and the portion which did not liquefy was collected in a large gas-holder. This, together with fresh supplies of air, was repeatedly circulated through the apparatus, with the object of making a preliminary concentration of the lighter portions. To avoid contamination with hydrogen, the gas-holder was well painted inside and the compressor cylinders lubricated with very dilute alkali. The total quantity of air dealt with in this operation amounted to about 73,500 litres.

A second fractionation of the gas thus collected was obtained by liquefying about 70 or 80 litres at a time in a glass bulb immersed in liquid air boiling under reduced pressure.* Light fractions were boiled off and the process repeated several times until the volume was reduced to 4700 c.c. This portion (1) was separated, by the method of absorption in cooled charcoal, into three fractions, (2) not absorbed at about $-190°$ C., (3) not absorbed at about $-110°$ C., (4) discarded. Spectroscopic examination showed (2) to be almost pure neon and helium with faint hydrogen lines. An attempt was made to fractionate (2) and (3) at the temperature of liquid air boiling at ordinary pressure ($-190°$ C.), but, in the case of (3), the fractions always showed the nitrogen spectrum (see table of fractionations); it was therefore decided to work at the temperature of liquid air boiling under reduced pressure, which represents a temperature of about $-205°$ C.

Table of Fractionations.



* A description of this piece of apparatus and its use has been given by Ramsay and ravers, 'Phil. Trans.,' A, vol. 197, 1901, p. 58.

Spectroscopic examination showed (5) and (6) to be chiefly neon and helium, with a little hydrogen—no new lines were detected; (7) was neon and nitrogen, while (8) and (11) consisted chiefly of nitrogen; (5), (6), (7) were mixed and separated into the fractions; (14) pumped off at −205° C., (15) at −190° C., (16) and (17) at 18° C., and (18) at 236° C.; (8), (9), (10) were mixed and similarly separated into fractions (19), (20), (21); (19) gave the nitrogen spectrum, (14) and (15) consisted of neon and helium; (16) and (17) contained hydrogen in addition to neon and helium, while (18) contained more nitrogen than neon. Fractions (14), (15), (16), (17) were therefore analysed for hydrogen, whilst the remaining fractions, as shown by the table, were worked up for neon and helium, of which 25 c.c. were obtained. The gases were measured separately, sparked with oxygen, the excess of which was subsequently withdrawn by means of phosphorus. The diminution in volume gave the amount of hydrogen present. The gases were measured by the method described by Ramsay.*

	c.c.		c.c.
Volume of (14).....	1·258	Volume of (15).....	1·995
„ after sparking	1·260	„ after sparking	2·001
„ of hydrogen...	nil	„ of hydrogen...	nil

N.B.—The slight increase in volume represents a small error of measurement of the order about 1 in 400.

	c.c.		c.c.
Volume of (16).....	11·615	Volume of (17).....	6·507
„ after sparking	11·420	„ after sparking	5·924
„ of hydrogen...	0·195	„ of hydrogen...	0·583

Total volume of hydrogen..... 0·778 c.c.

The spectra of (14), (15), (16), (17) were very carefully compared with the spectrum of a neon and helium tube, and they agreed exactly throughout; no new lines could be detected; this also shows that the contractions could not have been due to the presence of carbon monoxide, possibly derived from the charcoal. Any hydrocarbons in the air would have been removed in the charcoal.

As a test of this method of separating a small proportion of hydrogen from air, a parallel series of fractionations was performed on about 60 litres of air, to which 5·6 c.c. (measured to 0·1 c.c.) of hydrogen had been added. Three fractions were finally obtained from charcoal: (1) at −205° C., (2) and (3) at −190° C. Analysis, as before, gave the following results:—

* 'Roy. Soc. Proc.,' A, vol. 76, 1905, p. 113.

(1)	4·602 c.c.	gave	0·170 c.c.	hydrogen (3·7 per cent.).
(2)	13·005	„	0·702	„ (5·4 „).
(3)	29·259	„	1·585	„ (5·4 „).

Total volume of hydrogen..... 2·457 c.c.

Thus, only about half the added hydrogen was recovered. The most probable source of loss seems to be in the fractionation from the liquefied gas, when even the passage of air bubbles through the liquid appears insufficient to expel all the hydrogen. Dewar has also stated* that hydrogen is very soluble in liquid air; it is thus possible that a little hydrogen might have been removed during the initial process with the liquefying machine. It is noteworthy that the fraction pumped from the charcoal at −205° C. contains less hydrogen than that which comes off at −190° C.; the absorption of hydrogen seems to be of about the same order as that of neon.

The total volume of hydrogen obtained from the air was 0·778 c.c., and the total volume of mixed neon and helium was 46 c.c. Using the estimate of Ramsay,† agreeing with the previous one of Dewar,‡ viz., 60,000 volumes of air contain 1 volume of neon and helium together, it is found that 2,760,000 c.c. of air contain 46 c.c. of neon and helium and 0·778 c.c. of hydrogen, whence 3,550,000 c.c. of air contain 1 c.c. of hydrogen. This number can be corrected by assuming, as an approximate factor, the ratio 2·5/5·6 derived from the experiments on the air to which hydrogen had been introduced. The corrected estimate is 1 c.c. of hydrogen in 1,583,600 c.c. of air, or, approximately, one volume of hydrogen per million and a half volumes of air.

On comparing the total volume of air originally dealt with, it is evident that the liquefying plant was of very little use in concentrating the lightest portions; it is certainly better to calculate the hydrogen on the quantity of neon and helium actually obtained than on the original volume of air.

It appears from these results that the proportion of free hydrogen in the atmosphere is exceedingly small—so small, indeed, as to make its exact estimation a matter of extreme difficulty, and we must regard our results as indicating the order rather than the exact proportion in which the hydrogen is present.

In conclusion, I wish to express my warmest thanks to Sir William Ramsay, who suggested and constantly superintended the work during its progress.

* *Loc. cit.* † *Loc. cit.* ‡ *Loc. cit.*